



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



Publication number: **0 605 142 A1**

12

## EUROPEAN PATENT APPLICATION

21 Application number: 93310114.9

51 Int. Cl. 5: **B01J 23/02, B01J 23/04,  
B01J 27/18, B01J 37/02,  
C08G 77/08**

22 Date of filing: 15.12.93

30 Priority: 31.12.92 GB 9227152

43 Date of publication of application:  
06.07.94 Bulletin 94/27

84 Designated Contracting States:  
DE FR GB

71 Applicant: **DOW CORNING LIMITED**  
Cardiff Road  
Barry  
South Glamorgan CF63 2YL Wales(GB)

72 Inventor: **Kolaczowski, Stanislaw T.**  
Park House,  
Park Gardens  
Bath(GB)  
Inventor: **Serbetcioğlu, Serpil**  
6 Marlborough Buildings  
Bath(GB)  
Inventor: **Perera, Semali**  
9 Pines Way,  
Radstock  
Bath(GB)

74 Representative: **Vandamme, Luc Johan Roger**  
Dow Corning Limited  
Cardiff Road  
Barry South Glamorgan CF6 7YL Wales (GB)

54 **Process for coating a ceramic monolith support with a catalyst.**

52 A process of coating or loading a ceramic monolithic catalyst support with a heterogeneous water soluble catalyst comprises making a slurry of the catalyst in a mixture of from 2 to 50% by weight of water and from 98 to 50% of a liquid organic carrier, applying the slurry onto the surface of the monolithic catalyst support and allowing the slurry to dry by evaporation of the mixture of water and liquid organic carrier.

EP 0 605 142 A1

This invention is concerned with a process for loading a ceramic monolith with catalyst. It is particularly related to a process for loading a ceramic monolith with heterogeneous water soluble catalysts.

Monolithic catalyst supports, or monoliths, are known in the art and have been described in many publications, e.g. Advanced Materials in Catalysis, Materials Sciences Series, 77, pages 293 to 324. They are traditionally mainly used for gaseous reactions, e.g. in automotive emission control systems, as described e.g. in E.P. specifications 443 905 and 460 388. Some applications involving a liquid phase are also reported. These have been done in a three phase monolithic reactor and are limited in the prior art to hydrogenation reactions, including hydrogenation of aqueous nitrobenzoic acid,  $\alpha$ -methylstyrene, 2-ethylhexenal and anthraquinones. Monolithic catalyst supports may be made from any material which will not react with any of the reagents, catalysts or reaction products, except where the catalyst itself forms part of the monolithic catalyst support structure. Traditional materials used for manufacturing monolithic catalyst supports include ceramics, metals, alloys, plastics, resins and even the heterogeneous catalyst itself or a mixture thereof with an inert binder.

Loading of monolithic catalyst supports with a number of catalyst has been described in several publications. The methods which have been described include catalyst incorporation during the manufacture of the monolithic catalyst supports, deposition of active material directly onto the monolithic catalyst support, washcoating, i.e. laying down a high surface area coating onto which the catalyst is deposited or depositing the washcoat and the catalyst at the same time.

It has been proposed e.g. in G.B. 1 600 588-A, to prepare catalysts by intimately admixing a solid, base metal component with a solid alumina support component preferably with a liquid containing a soluble or dispersed form of a catalytically active platinum group metal, followed by depositing these components on a macrosized carrier, e.g. a monolith. The alumina support is used as wash-coat to increase the size of the surface on which the catalyst is deposited. In the Derwent abstract of JP 4110038 a catalyst is deposited on a honeycomb using a mixture of gypsum, kaoline, titanium oxide and glass fibre as a wash-coat.

In many cases the active catalyst was obtained by applying a solution of the salt of the catalyst followed by further reacting the salt in order to form the active catalyst species *in situ*, e.g. by oxidation or precipitation. The present invention has the aim to provide a coating of the catalyst without having to change the nature of the deposited material and without the need for a wash-coat.

Although many of the methods of loading the monolithic catalyst supports work adequately for many applications, it was observed that where water soluble heterogeneous catalysts are to be loaded the known methods tend to give a coating which does not give good uniform adhesion and good appearance.

We have now found that if the heterogeneous water soluble catalysts are loaded by using a mixture of water and organic liquid carriers, a better coating of the catalyst with improved adhesion to the monolith and improved appearance is achieved.

According to the invention there is provided a process of loading a ceramic monolithic catalyst support with a heterogeneous water soluble catalyst, which comprises making a slurry of the catalyst in a mixture of from 2 to 50% by weight of water and from 98 to 50% of a liquid organic carrier, applying the slurry onto the surface of the monolithic catalyst support and allowing the slurry to dry by evaporation of the mixture of water and liquid organic carrier.

The present invention is only concerned with the use of ceramic monolithic catalyst supports. Useful materials for making ceramic monolithic catalyst supports include aluminates, silicates, aluminosilicates, natural clays, cordierite, zirconia, barium titanate and silicon carbide. Ceramic monolithic catalyst supports may be made in any of the well known manners but are usually produced by moulding, extrusion or corrugation methods, which methods are well known in the art and have been described in several publications.

The monolithic catalyst supports are composed of one or more channels. If more than one these channels are usually parallel, or at least substantially parallel, to each other, and may be circular, hexagonal, square, triangular or irregular in section. The shape of the section of the channels is not important but is usually of a symmetric type as a result of the manufacturing process. The channel sections do not even have to have a consistent section for the total length of the channel. They may for example have an increasing diameter or an irregularly changing diameter over the length of the monolithic catalyst support. The use of the word diameter does not limit the channels to ones with circular sections as it indicates only a measure of the hollow of the channel. Preferably, however, the channels have a constant section shape and size for the total length of the monolithic catalyst support.

Preferred monolithic catalyst supports are those which are useful in polymerisation reactions, particularly polymerisation of organosilicon compounds. The polymerisation process using such monoliths forms the subject of a co-pending patent application. These preferred monolithic catalyst supports may have a channel diameter which is conveniently in the range of from 0.1 to 50mm, preferably from 1 to 30mm, more

preferably from 3 to 10mm. The number of channels provided in the monolithic catalyst support may vary depending on the desired output of the polymerisation reaction, the available area in the reactor in which the support is to be placed and the feeding method and facilities of the reactor. It is, however, envisaged that the preferred total area of monolithic catalyst supports, measured in section, would be equivalent to that of a circle with a diameter in the range of from 150mm to 50,000mm, more preferably 500 to 5000mm, most preferably 1000 to 3000mm.

The thickness of the monolithic catalyst support channel sides will effect the mechanical strength of the monolithic catalyst support. For the preferred ceramic monolithic catalyst supports the total bed voidage, i.e. the ratio of free space over space taken up by the material making up the support per unit of volume, is in the range of from 0.3 to 0.95, preferably from 0.5 to 0.8, most preferably 0.6 to 0.75.

The length of the monolithic catalyst support, i.e. its size in the direction of the flow of the reagents, could vary widely depending on the required residence time of the reagents with the catalyst, the operating temperature, the activity of the catalyst, the density of the catalyst on the surface of the monolithic catalyst support, the desired outcome of the reaction and the physical properties of the reagents and/or the reaction product. The preferred monolithic catalyst supports are provided in blocks with limited length, e.g. from 5 to 1000mm, preferably 100 to 500mm, and to place a number of these blocks on top of each other. In this way it becomes possible to provide a monolithic catalyst support system with a number of channels with varying diameter throughout the reactor. It is for example conceivable to have smaller channel diameters at the top of the reactor, where the reagents enter the reactor, and to increase the diameter further down the reactor to accommodate a reaction product of increasing viscosity. It is expected that in commercial situations the total length of the monolithic catalyst supports used in a reactors would be in the range of from 150mm to 50,000mm, more preferably 500 to 5000mm, most preferably 1000 to 3000mm.

Heterogeneous water soluble catalysts for use in the process of the invention are catalysts which are solid at room temperature and normal atmospheric conditions, which are soluble in water and are useful in catalysing liquid phase, gas phase or 2-phase liquid/gas reactions. Particularly preferred are heterogeneous catalysts which catalyse the production of organosilicon compounds by polymerisation of organosilicon monomers or oligomers. The production of organosilicon polymeric compounds, by the polymerisation or co-polymerisation of relatively low molecular weight organosilicon compounds, is a well known step in the manufacture of commercial silicones. This process has been extensively described, e.g. for the production of organopolysiloxanes, and may include equilibration, condensation and/or addition reactions. Heterogeneous catalysts for such reactions are also well known and have been described in the literature.

Potential heterogeneous polymerisation catalysts include condensation, addition and equilibration catalysts. They have been described in a number of publications and many are commercially available. Suitable catalysts are exemplified by carboxylates of rubidium or caesium, hydroxides of magnesium, barium or strontium, borates, acetates and phosphates, e.g.  $\text{Ba}(\text{OH})_2$ ,  $\text{Sr}(\text{OH})_2$ ,  $\text{Na}_2\text{B}_4\text{O}_7$ ,  $\text{CsOAc}$ ,  $\text{K}_3\text{PO}_4$ ,  $\text{Na}_3\text{PO}_4$ ,  $\text{KBO}_2$  and other catalysts as mentioned in the art, e.g. in G.B. patent specification 2,256,872.

The process of the invention requires the formation of a slurry of the catalyst and a mixture of water and a liquid organic carrier. Preferably no other ingredients are used in the slurry. The liquid organic carrier may be one or more of an organic hydrocarbon, alcohol, aldehyde, ether or ketone which carrier preferably has a boiling point at standard atmospheric pressure (1000 mbar) of no more than 150°C. The liquid organic carrier is preferably a liquid which will not, or at most only sparingly, dissolve the catalyst as this will make the formation of a slurry easier. It may be a mixture of more than one liquid organic carriers. It is more preferred that the liquid carrier has a boiling point at 1000 mbar of no more than 100°C. At least 2% by weight of the mixture of water and liquid organic carrier is to be water, and at least 50% by weight of said mixture is to be taken up by the liquid organic carrier. Preferably from 5 to 20% by weight of the mixture is water. Particularly preferred liquid organic carriers are lower alkanols, i.e. those having less than 6 carbon atoms, e.g. methanol, ethanol and isopropanol.

The slurry has preferably the consistency of a paste at the temperature and conditions of loading the ceramic monolithic catalyst support. The slurry can be prepared by mixing a powder form of the catalyst with the mixture of water and the liquid organic carrier till the desired consistency is achieved. If the liquid organic carrier is very volatile it is of course desirable to maintain the slurry in an atmosphere where the amount of evaporation is reduced to a minimum. Depending on the ingredients the slurry may comprise from 20 to 70% of the catalyst, preferably 30 to 50%, most preferably 35 to 45%.

In the process of the invention, the slurry is then applied to the surface of the monolithic catalyst support. This may be done in any convenient way, e.g. by standard coating techniques. Suitable techniques include dip coating, flow coating, brushing and spraying.

Once the slurry has been applied to the monolithic catalyst support, it is allowed to dry by evaporation of the mixture of water and liquid organic carrier. This may be achieved by exposing the coated support to

atmospheric conditions. Where the catalyst is susceptible to degradation under such conditions alternative conditions may apply. These include the use of an inert gas atmosphere. Evaporation of the mixture of water and the liquid organic carrier may be accelerated e.g. by the use of heat or a gas flow. Best results have been achieved by allowing the majority of the mixture of water and the liquid organic carrier to evaporate at relatively lower temperatures, e.g. room temperature (around 20 °C) or up to, but not including, the temperature at which the mixture of water and the liquid organic carrier boils, followed by heating the coated monolith at higher temperatures.

It is preferred to coat the monolithic catalyst support with the catalyst in such a way that a reasonably uniform coating of the catalyst is provided, i.e. where the loading of catalyst per unit area of the support is fairly constant on average. Although it is preferred to cover the surface catalyst, a patchy or patterned coating could also be used. It is particularly preferred to provide a coating which is rough to some extent, as this would increase the surface area of the catalyst bed, and hence the reactivity of the loaded monolithic catalyst support. A minimum thickness of catalyst layer would be equivalent to a molecular monolayer of the catalyst. There is no theoretical maximum thickness of the catalyst layer, although practical considerations have to be taken into account. These include the remaining empty volume in the channels of the monolithic catalyst support, the adhesion strength of the catalyst to the support as well as any cost considerations. A preferred average thickness would be in the range of from 0.05 to 2mm, preferably 0.1 to 1mm. The different results can be achieved to some extent by using different conditions in which the evaporation of the mixture of water and the liquid organic carrier is carried out. For example a faster initial drying or heating, above the boiling point of the mixture of water and the liquid organic carrier, will more likely result in a rougher coating. A very slow evaporation will result in a more uniform and smooth coating.

There now follow a number of examples in which the invention is illustrated in more detail.

A monolithic catalyst support tube was made from Pormulit® alumina silicate having an inner diameter of 15mm, a channel wall thickness of 2.5mm and a length of 740mm. The monolithic catalyst support was prepared for coating with tripotassium phosphate catalyst by washing the monolithic catalyst support tube with distilled water and drying it for 2 hours at 120 °C.

A slurry was prepared according to Table I, of which some are examples according to the invention and some (C) comparative examples. The liquid organic carrier was 99.5% by weight pure material. The slurry was poured through the monolith tube to coat the inside of the channel to a height of 500mm. The monolith tube was then dried in a nitrogen atmosphere at room temperature for two hours, followed by drying in an oven at 100 °C for a further hour.

TABLE I

Example	Mixture Components	
	Water (in % by weight)	Organic Liquid (type)
1	5	n-heptane
2	20	n-heptane
3	25	toluene
4	25	pentanol
5	25	diethyl ether
6	5	ethanol
7	20	ethanol
8	50	ethanol
9	15	formaldehyde
10	15	acetone
11	15	n-butanol
C1	0	n-heptane
C2	0	toluene
C3	0	pentanol
C4	0	diethyl ether
C5	0	ethanol
C6	100	—

The appearance and adhesion of the catalyst to the monolithic support was visually inspected. It was found that all the Example coatings (1 to 11) had good adhesion to the walls of the monolith tube and gave a fairly uniform slightly rough coating. All the comparative examples (C1-C6) had major flaws in the coating and peeled away from the walls.

#### Claims

1. A process of loading a ceramic monolithic catalyst support with a heterogeneous water soluble catalyst which comprises making a slurry of the catalyst, applying the slurry onto the surface of the monolithic catalyst support and allowing the slurry to dry, characterised in that the slurry is prepared by mixing the catalyst with a mixture of from 2 to 50% by weight of water and from 98 to 50% of a liquid organic carrier.
2. A process according to Claim 1 further characterised in that the slurry consist of 30 to 50% by weight of the catalyst and 50 to 70% by weight of the mixture of water and the liquid organic carrier.
3. A process according to Claim 1 or Claim 2 further characterised in that the liquid organic carrier consists of one or more of an organic hydrocarbon, alcohol, aldehyde, ether or ketone which carrier has a boiling point at standard atmospheric pressure (1000 mbar) of no more than 150 °C.
4. A process according to any one of the preceding claims further characterised in that the catalyst is insoluble in the liquid organic carrier.
5. A process according to any one of the preceding claims further characterised in that the mixture of water and the liquid organic carrier contains from 5 to 20% by weight of water.
6. A process according to any one of the preceding claims further characterised in that the liquid organic carrier is a lower alkanol having less than 6 carbon atoms.
7. A process according to any one of the preceding claims further characterised in that the slurry has the consistency of a paste at the temperature and conditions of loading the ceramic monolithic catalyst support.
8. A process according to any one of the preceding claims further characterised in that the slurry is applied to the surface of the monolithic catalyst support by dip coating, flow coating, brushing or spraying.
9. A process according to any one of the preceding claims further characterised in that drying of the slurry is effected by the evaporation of the mixture of water and the liquid organic carrier through exposure of the coated support to heat or to a gas flow.
10. A process according to any one of the preceding claims further characterised in that drying the slurry is effected by allowing the majority of the mixture of water and the liquid organic carrier to evaporate at relatively lower temperatures, followed by heating the coated monolith at higher temperatures.



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 93 31 0114

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cls.)
X	US-A-4 065 510 (SCHREYER ET AL.) * column 2, line 18 - line 61 * * column 4, line 49 - line 53 * * claims 1-3 *	1-10	B01J23/02 B01J23/04 B01J27/18 B01J37/02 C08G77/08
A	EP-A-0 503 825 (DOW CORNING) * page 4, line 18 - line 45 * * claims *	1-10	
P,A	EP-A-0 560 074 (CORNING INC.) * page 2, line 27 - line 41 * * page 3, line 8 - line 25 * * page 7; examples 1,2 * * claims 1-13 *	1-10	
D,A	FR-A-2 663 941 (DOW CORNING)		
A	FR-A-2 218 138 (CORNING GLASS)		
			TECHNICAL FIELDS SEARCHED (Int.Cls.)
			B01J C08G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 18 April 1994	Examiner Lo Conte, C
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document	